

UNCLASSIFIED

AD **409 823**

DEFENSE DOCUMENTATION CENTER

FOR

SCIENTIFIC AND TECHNICAL INFORMATION

CAMERON STATION, ALEXANDRIA, VIRGINIA



UNCLASSIFIED

NOTICE: When government or other drawings, specifications or other data are used for any purpose other than in connection with a definitely related government procurement operation, the U. S. Government thereby incurs no responsibility, nor any obligation whatsoever; and the fact that the Government may have formulated, furnished, or in any way supplied the said drawings, specifications, or other data is not to be regarded by implication or otherwise as in any manner licensing the holder or any other person or corporation, or conveying any rights or permission to manufacture, use or sell any patented invention that may in any way be related thereto.

63 4-2

OFFICE OF NAVAL RESEARCH

Contract Nonr 2687(00)

Task No. NR 356-408

TECHNICAL REPORT NO. 38

A New Class of Double-Bridged Coordination
Polymers Based On Chromium(III)

by

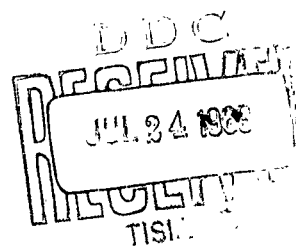
A. J. Saraceno and B. P. Block

Accepted by the Journal of the American Chemical Society

PENNSALT CHEMICALS CORPORATION
Research and Development Department
Wyndmoor, Pennsylvania

June 1963

Reproduction in whole or in part is permitted for
any purpose of the
United States Government



CATALOGED BY DDC
AS AD No. _____

409823

409 823

A New Class of Double-Bridged Coordination Polymers Based on Chromium(III)

Sir:

Earlier reports from this laboratory have concerned the preparation of coordination polymers of types which we write symbolically as $[M(AB)X_2]_n^{(1)}$ and $[MX_2]_n^{(2)}$ where AB represents a uninegative bidentate ligand and X repre-

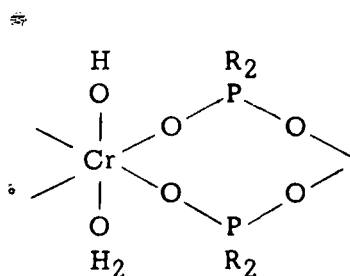
1. B.P. Block, J. Simkin, and L.R. Ocone, J. Am. Chem. Soc. 84, 1749 (1962).
 2. B.P. Block, S.H. Rose, C.W. Schaumann, E.S. Roth, and J. Simkin, Ibid. 3200.
-

sents a uninegative bridging group. We now wish to report a third class, $[M(a)(b)X_2]_n$, where a represents a neutral unidentate ligand and b a uninegative ligand. The preparation of this new class differs in method from that in the earlier series and appears to lead to polymers with substantially higher molecular weight than we have found for the other two types. The non-bridging ligands a and b are inorganic, so that this material is an example of a coordination polymer which in addition to its inorganic backbone has inorganic blocking groups in the repeating unit.

The synthesis is a two-step process in which chromium(II) acetate is treated with a potassium phosphinate ($KOPR_2O$) to yield the corresponding chromium(II) phosphinate ($R=C_6H_5$, I). The latter is then oxidized with air in the presence of water to yield the composition $Cr(H_2O)(OH)(OPR_2O)_2$ ($R=C_6H_5$, II) which has polymeric properties. II has been prepared by these reactions under a variety of conditions, but here we will only describe a set of conditions which gives a product exhibiting a high intrinsic viscosity in chloroform.

A suspension of 2.7 g. of freshly prepared $\text{Cr}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ in 125 ml. of deoxygenated water is refluxed under nitrogen with stirring for 1 hr. After the addition of a deoxygenated solution of $\text{KOP}(\text{C}_6\text{H}_5)_2\text{O}$ (prepared by the exact neutralization of 8.0 g. of $(\text{C}_6\text{H}_5)_2\text{P}(\text{O})\text{OH}$ with 1 M. KOH) without exposure to air, the refluxing is continued for 2-3 hr. under nitrogen. The precipitated intermediate I is then separated by filtration at room temperature and washed several times with deoxygenated water, all operations being conducted under nitrogen. I is next dispersed in 500 ml. of water and oxidized to II by exposure to the atmosphere. After crude II has been removed by filtration, washed thoroughly with water, and dried at 100° , it is dissolved in benzene. The resulting solution is then separated from the small quantity of benzene insolubles (less than 0.3 g.) by filtration and evaporated at room temperature in a stream of nitrogen to yield II. Final drying is at 120° . Anal. Calcd. for $\text{C}_{12}\text{H}_{13}\text{CrO}_6\text{P}_2$: C, 55.25%; H, 4.43%; Cr, 10.0%; P, 11.88%. Found: C, 56.39%; H, 4.36%; Cr, 9.7%; P, 11.93%. Yields vary from 70 to 95%. The intrinsic viscosity of II prepared in this manner is 0.6 to 0.7 in chloroform. Less rigorously controlled conditions lead to polymers with intrinsic viscosities from 0.1 to 0.5. Even unfractionated samples with intrinsic viscosities in the range 0.12 to 0.20 have number average molecular weights greater than 10,000 as determined by ebulliometry and vapor pressure osmometry in chloroform. Consequently the higher-viscosity samples certainly have molecular weights of at least several tens of thousands.

Although any of the groups present in II could serve as bridging groups, the most probable structure contains a double-bridged backbone similar to that suggested for $\text{Cr}(\text{AcCHAc})(\text{OP}(\text{C}_6\text{H}_5)_2\text{O})_2$ ¹ except that a *cis* configuration is not required. The infrared spectrum of II contains absorption peaks characteristic of PO_2 stretching with virtually the same frequency and absorption profile as found for polymeric $\text{Cr}(\text{AcCHAc})(\text{OP}(\text{C}_6\text{H}_5)_2\text{O})_2$ ¹. This is strong evidence that the diphenylphosphinate anion is functioning in the same way in both polymers. Furthermore, the hydroxyl group and the water O-H stretching vibrations can be identified separately at frequencies which suggest they are normally coordinated groups. Thus infrared indicates that the hydroxyl groups are not bridging groups. The solubility of II in benzene or chloroform accompanied by marked swelling and the high intrinsic viscosity values are good evidence for the presence of linear chains as the predominating species with cross-linking only of minor importance. The indications are, then, that the repeat unit is



Thermogravimetric analysis of II shows initial weight loss at 375° with a step in the 410-430° region which corresponds to a 3-10% weight loss. No

polymer melt temperature has been observed up to or well beyond the decomposition point. Surprisingly the polymer shows remarkable resistance to hydrolysis and other chemical degradation. For example, no change in intrinsic viscosity is observed upon refluxing a suspension of the polymer in water for several hours. A cast film of high-viscosity II plasticized with 30% Aroclor 1254 has a tensile strength of over 1900 p.s.i.

In addition to the diphenyl species described here we have also been able to prepare the analogues with phenylmethylphosphinate, dimethylphosphinate, and cacodylate bridging groups. The mechanism by which this kind of polymer forms is not clear. It would appear that the intermediate I could be a polymer somewhat analogous to the phosphinate polymers involving zinc, beryllium, and cobalt². The oxidation step then may merely serve to increase the oxidation state of the chromium and introduce the additional ligands. Alternatively polymerization may be involved in the oxidation step.

Acknowledgment. This investigation was supported in part by the Office of Naval Research. We are indebted to several of our colleagues for assistance with various experiments. Analytical data were supplied by our Analytical Department.

Research and Development Department
Pennsalt Chemicals Corporation
Wyndmoor, Pennsylvania

A.J. Saraceno
B.P. Block

TECHNICAL REPORT DISTRIBUTION LIST

Pennsalt Chemicals Corporation

Contract No. Nonr 2687(00)		NR 356-408	
No. of Copies		No. of Copies	
Commanding Officer Office of Naval Research Branch Off. The John Crerar Library Building 86 East Randolph Street Chicago 1, Illinois (1)	U.S. Army Chemical Research and Development Laboratories, Technical Library Army Chemical Center, Maryland (1)	Professor A.R. von Hippel Department of Physics Massachusetts Institute of Technology Cambridge 38, Massachusetts (1)	
Commanding Officer Office of Naval Research Branch Off. 346 Broadway New York 13, New York (1)	Office of Technical Services Department of Commerce Washington 25, D.C. (1)	Dr. S. Young Tyree, Jr. Department of Chemistry University of North Carolina Chapel Hill, North Carolina (1)	
Commanding Officer Office of Naval Research Branch Off. 1030 East Green Street Pasadena 1, California (1)	Dr. P. A. Miller Office of Naval Res. Br. Off. 1000 Geary Street San Francisco 9, California (1)	Dr. J.C. Bailar, Jr. Department of Chemistry University of Illinois Urbana, Illinois (2)	
Commanding Officer Office of Naval Research Branch Off. Box 39 Navy #100 Fleet Post Office New York, New York (7)	Dr. C. Haber Naval Ordnance Laboratory Corona, California (1)	Dr. A.B. Burg Department of Chemistry University of Southern Calif. Los Angeles 7, California (2)	
Director, Naval Research Lab. Washington 25, D.C. Attn: Technical Information Officer Chemistry Division (6) (2)	Dr. Porter W. Erickson Chemistry Research Department Non-Metallic Materials Division Room 4-171 Naval Ordnance Laboratory White Oak, Maryland (1)	Dr. L. F. Audrieth Department of Chemistry University of Illinois Urbana, Illinois (2)	
Chief of Naval Research Department of the Navy Washington 25, D.C. Attn: Code 425 (10)	Dr. Albert Lightbody Naval Ordnance Laboratory White Oak, Maryland (1)	Dr. R. Pepinsky Crystallographic Lab. Department of Physics Penna. State University University Park, Pennsylvania (1)	
Technical Director Research & Eng'g. Division Off. of the Quartermaster Gen'l Department of the Army Washington 25, D.C. (1)	Naval Ordnance Test Station China Lake, California Attn: Head, Chemistry Division Code 40 Code 50 (1) (1)	Dr. O. Williams National Science Foundation Washington 25, D.C. (1)	
DDR&E Technical Library Room 3C-128, The Pentagon Washington 25, D. C. (1)	Commanding Officer and Director U.S. Naval Civil Engineering Lab. Port Hueneme, California Attn: Chemistry Division (1)	Dr. J. F. Pask Director of Mineral Technology University of California Berkeley, California (1)	
Research Director Clothing & Organic Materials Division Quartermaster Research & Engineering Command U. S. Army Natick, Massachusetts (1)	Dr. A. L. Powell Office of Naval Research Br. Off. 495 Summer Street Boston 10, Massachusetts (1)	Dr. A. T. Gwathmey Department of Chemistry University of Virginia Charlottesville, Virginia (1)	
Air Force Off. of Scientific Res. (SRC-E) Washington 25, D.C. (1)	Aeronautical Systems Division ASRCNP Wright-Patterson Air Force Base Ohio (1)	Dr. J. R. Goldsmith Department of Geology University of Chicago Chicago 35, Illinois (1)	
Commanding Officer Diamond Ordnance Fuze Labs. Washington 25, D.C. Attn: Tech. Information Office Branch 012 (1)	Director, Naval Research Lab. Washington 25, D. C. Attn: Code 6120, Attn: Dr. R. B. Fox (1) Code 6120, Attn: Mr. J.E. Cowling (1) Code 6120, Attn: Dr. A.L. Alexander (1) Code 6120, Attn: Dr. D.L. Venezky (1) Code 6210, Attn: Mr. J.A. Kles (1) Code 6110, Attn: Mr. E.J. Kohn (1)	Dr. Riley Schaeffer Department of Chemistry Indiana University Bloomington, Indiana (1)	
Office, Chief of Research & Development Department of the Army Washington 25, D. C. Attn: Physical Sciences Division (1)	Dr. H. C. Clark Department of Chemistry University of British Columbia Vancouver, British Columbia CANADA (1)	Dr. T. G. Fox, Director of Research Mellon Institute, 4400 Fifth Avenue Pittsburgh 13, Pennsylvania (1)	
Chief, Bureau of Ships Department of the Navy Washington 25, D.C. Attn: Code 342C Code 634C (2) (1)	Dr. E. G. Rochow Department of Chemistry Harvard University Cambridge 38, Massachusetts (1)	Aircraft Industries Association 7660 Beverly Boulevard Los Angeles 36, California Attn: Mr. H. D. Moran (10)	
Chief, Bureau of Naval Weapons Department of the Navy Washington 25, D.C. Attn: Technical Library Code: RRMA-3 (3) (1)	Dr. H. T. Smyth School of Ceramics Rutgers - The State University New Brunswick, New Jersey (1)	Chief, Bureau of Ships Department of the Navy Washington 25, D. C. Attn: Code 660L Mr. E.J. Hryckiewicz (1)	
ASTIA Document Service Center Arlington Hall Station Arlington 12, Virginia (10)	Dr. John E. Leffler Department of Chemistry Florida State University Tallahassee, Florida (1)	American Potash & Chem. Corp. 201 W. Washington Blvd. Whittier, California Attn: Dr. W.S. Emerson (2)	
Director of Research U.S. Army Signal Research & Development Laboratory Fort Monmouth, New Jersey (1)	Dr. William N. Lipscomb Department of Chemistry Harvard University Cambridge 38, Massachusetts (1)	U.S. Borax Research Corp. Anaheim, California Attn: Dr. Carl Randolph (2)	
Naval Radiological Defense Lab. San Francisco 24, California Attn: Technical Library (1)	Dr. T. D. Parsons Department of Chemistry Oregon State College Corvallis, Oregon (1)	General Electric Company Research Laboratory Attn: Dr. J. R. Elliot P.O. Box 1088 Schenectady, New York (2)	
Stanford Research Institute Menlo Park, California Attn: Mr. Maurice L. Huggins (1)	Dr. L. F. Rahn Princeton Plastics Laboratory Princeton University Princeton, New Jersey (1)	Dr. P.D. George General Electric Company General Engineering Laboratory Schenectady, New York (2)	
Commanding Officer Army Research Office Box CM, Duke Station Durham, North Carolina Attn: Scientific Synthesis Officer (1)	Dr. A. V. Tobolsky Department of Chemistry Princeton University Princeton, New Jersey (1)	Boeing Airplane Company Wichita 1, Kansas Attn: Library (1)	
Brookhaven National Laboratory Chemistry Department Upton, New York (1)	Dr. R. S. Stein Department of Chemistry University of Massachusetts Amherst, Massachusetts (1)	Dr. Hans B. Jonassen Department of Chemistry Tulane University New Orleans 15, Louisiana (1)	
Atomic Energy Commission Division of Research Chemistry Programs Washington 25, D. C. (1)		Dr. Henry Taube Department of Chemistry Stanford University Stanford, California (1)	

(over)

TECHNICAL REPORT DISTRIBUTION LIST (Cont.)

Pennsalt Chemicals Corporation

Contract No. Nonr 2687(00)

NR 356-408

	<u>No. of Copies</u>
Atomic Energy Commission Division of Technical Information Extension Post Office Box 62 Oak Ridge, Tennessee	(1)
Plastics Technical Evaluation Center Picatinny Arsenal Dover, New Jersey	(1)
John I. Thompson & Co. 1118 -22nd St., N.W. Washington, D.C. Attn: Mr. Carl A. Posey	(1)
Dr. M. S. Cohen, Chief Propellants Synthesis Section Reaction Motors Division Denville, New Jersey	(1)
Dr. M.J.S. Dewar Department of Chemistry University of Chicago Chicago 37, Illinois	(1)
Commanding Officer Ordnance Materials Res. Office Watertown Arsenal Watertown 72, Mass. Attn: RPD	(1)
Commanding Officer Rock Island Arsenal Rock Island, Illinois Attn: Mr. R. Shaw, Laboratory	(1)
Monsanto Research Corporation Everett Station Boston 49, Mass. Attn: Librarian	(1)
Dr. T. L. Heying Organics Division Olin Mathieson Chemical Corporation 275 Winchester Avenue New Haven, Connecticut	(1)
Dr. W. S. Fyfe Department of Geology University of California Berkeley, California	(1)
New York Naval Shipyard Material Laboratory Brooklyn 1, N. Y. Attn: Mr. B. B. Simms	(1)
Professor R. S. Nyholm University College London, Department of Chemistry Gower St., WC1 London, England	(1)
Monsanto Research Corporation 1515 Nicholas Road Dayton, Ohio Attn: Librarian	(1)
Mr. G. W. Harding Materials Officer Defense Research Staff British Embassy 3100 Massachusetts Ave., N.W. Washington 8, D.C.	(1)
Dr. Roald Hoffman Department of Chemistry Harvard University Cambridge 38, Mass.	(1)
The Dow Chemical Co. ARPA Laboratory 1710 Building Midland, Michigan	(1)
Naval Ordnance Test Station China Lake, California Attn: Code 4544 (Dr. Kaufmann) Code 5557 (Mr. S. H. Herzog- Mr. R.J. Landry)	(1)